

Supporting Information

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**Parallel Screening of Electrocatalyst Candidates using Bipolar
Electrochemistry**

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(10 pages)

Movie S1. This movie shows the operation of the Pd-Co BPE screening device. The frames shown in Figure 2 of the main text were extracted from this movie (avi format). Each frame of the movie represents 5.3 s of operation with the movie played at 2 fps. The duration of the application of E_{tot} was 5 min.

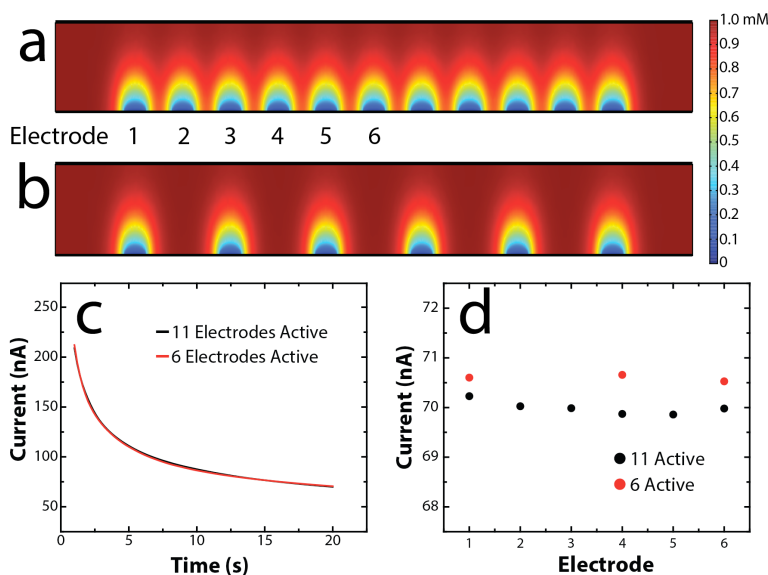


Figure S1. Evaluation of crosstalk in the array design. (a) 2D concentration profiles for the reversible reduction of a model species (O , $C^* = 1$ mM) after 20 s of operation under mass transport limited conditions in the same cell geometry used for the screening experiments discussed in the main text (cell height = 0.5 mm, cell width = 1 cm) when 11 electrodes ($325 \mu\text{m}$ width, $750 \mu\text{m}$ center-to-center separation) are active. (b) 2D concentration profiles for the same geometry as (a), but with only 6 electrodes are active. (c) Simulated current response vs. time for the electrodes in the model shown in (a) and (b). (d) Simulated current response at $t = 20$ s for the models shown in (a) and (b). The percent difference between the two models is less than 1%, demonstrating a low amount of electrochemical cross talk between electrodes in the array.

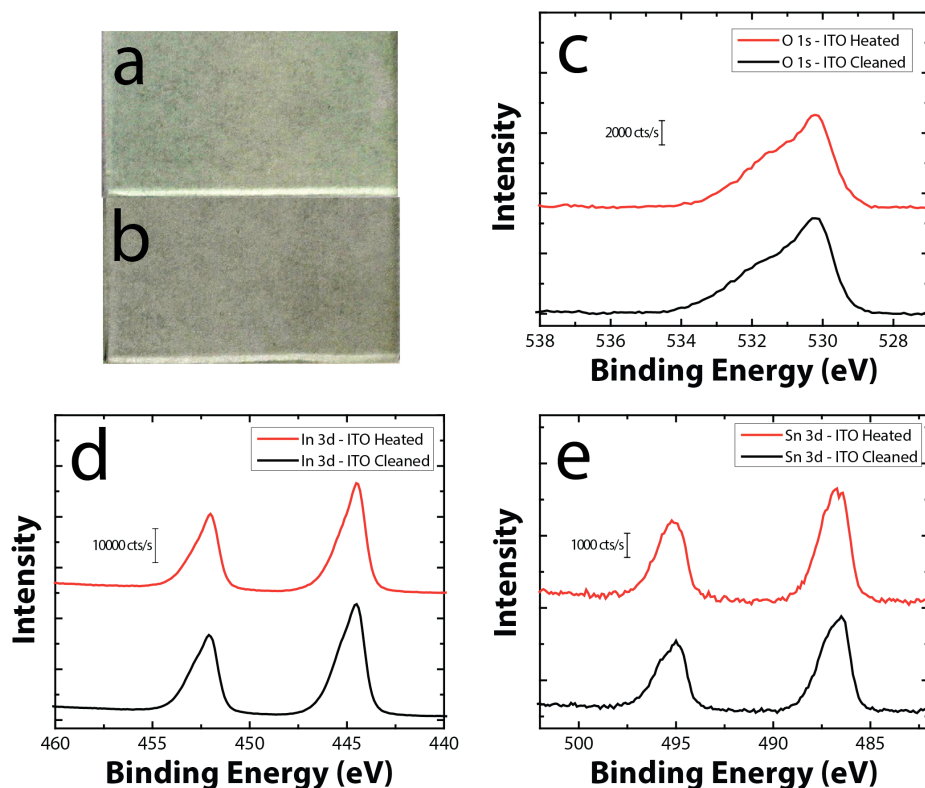


Figure S2. Effect of heating ITO to 350 °C 1.5 h in an atmosphere of 5% H₂/95% N₂. This is required to produce the electrocatalyst candidates. Optical images of an ITO-coated glass slide as received (a) and after heating (b). A slight color change is apparent, and four-point probe measurements of the two ITO coatings indicated a decrease of about 10% in sheet resistance after heating (before = 4.8 Ω/sq, after = 4.4 Ω/sq). (c-e) High-resolution XPS spectra of the ITO surface before (black) and after (red) heating: (b) O 1s, (c) In 3d, and (d) Sn 3d.

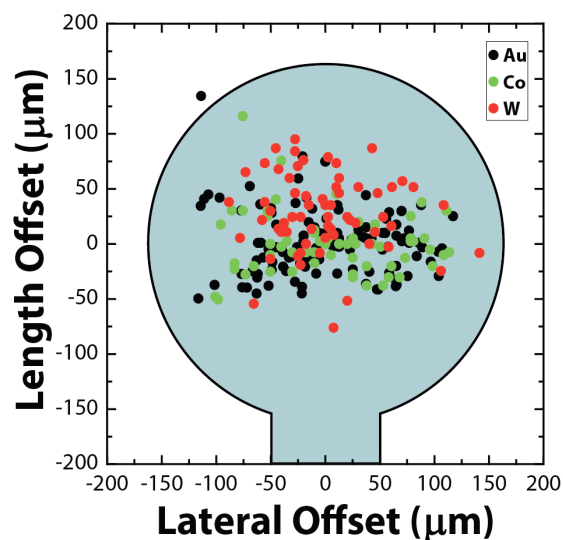


Figure S3. Spotting accuracy for 256 individual electrodes as determined from optical micrographs of BPE cathodes. The position indicates the centroid of the piezodispensed catalyst candidate relative to the center of the BPE cathodic pad.

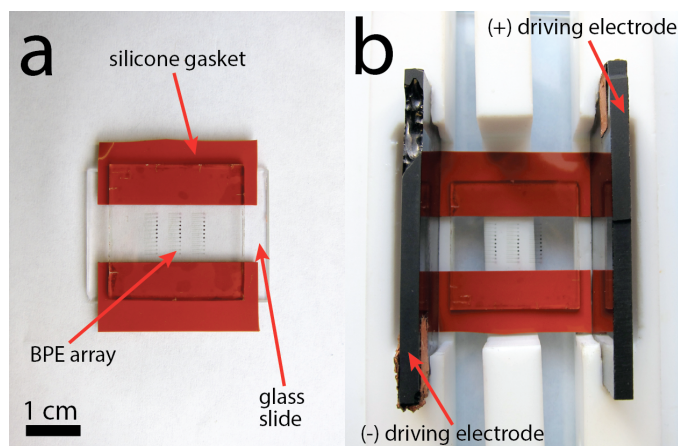


Figure S4. Photographs of the bipolar electrochemical cell used in these experiments. (a) The basic components of the cell that define the fluidic space. (b) The fully assembled cell, including the glassy carbon driving electrodes.

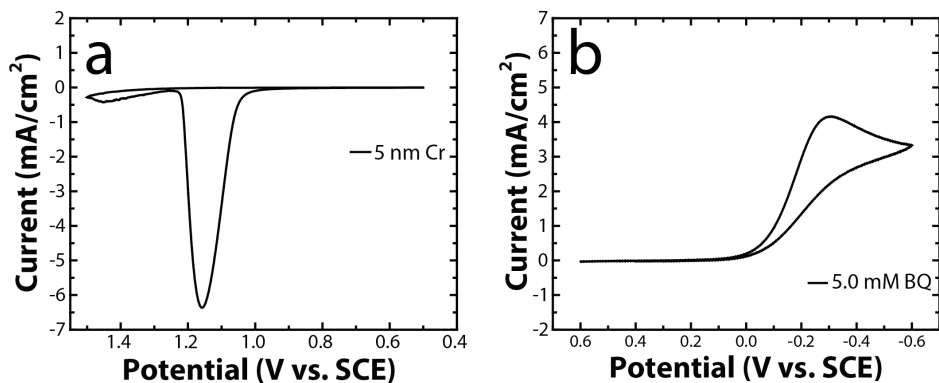


Figure S5. (a) Stripping voltammogram for a 5-nm thick Cr film deposited onto an ITO electrode. The electrolyte was 0.10 M H_2SO_4 and the scan rate was 50 mV/s. The onset potential (E_{onset}) is here defined as the potential when the current is 1% of the peak current, and it was determined to be 0.98 V vs. SCE. (b) Cyclic voltammogram for 5.0 mM BQ. The electrolyte solution was 0.10 M H_2SO_4 and the scan rate was 100 mV/s. E_{onset} for BQ reduction was determined to be 0.07 V vs. SCE.

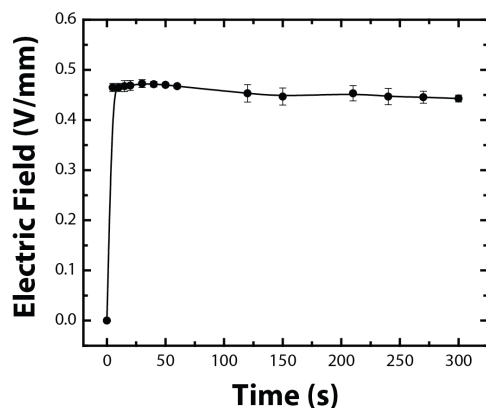


Figure S6. Electric field measurements showing the uniformity across the bipolar electrochemical cell. A cell configured with ten 100 μm -wide Au microbands separated by 1.25 mm center-to-center was placed in the bipolar electrochemical cell shown in Figure S3. The electrolyte was 0.10 M H_2SO_4 (same as the screening experiments). $E_{\text{tot}} = 15.0$ V was applied using a pair of glassy carbon driving electrodes and the potential difference between two electrodes separated by 3.75 mm center-to-center was measured using a digital multimeter (Keithley 6517B). The error bars indicate one standard deviation from the mean for three replicate experiments.

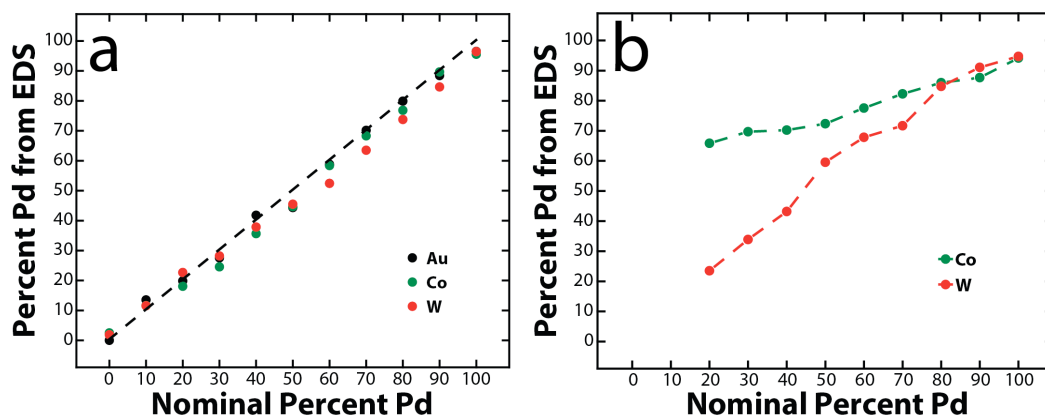


Figure S7. EDS analysis of spotted electrocatalyst candidates. Elemental compositions of the catalyst candidates were estimated (a) before and (b) after screening experiments. (b) Plot of relative at% Pd for Pd-Co and Pd-W vs. the nominal at% Pd dispensed onto the BPE cathode.

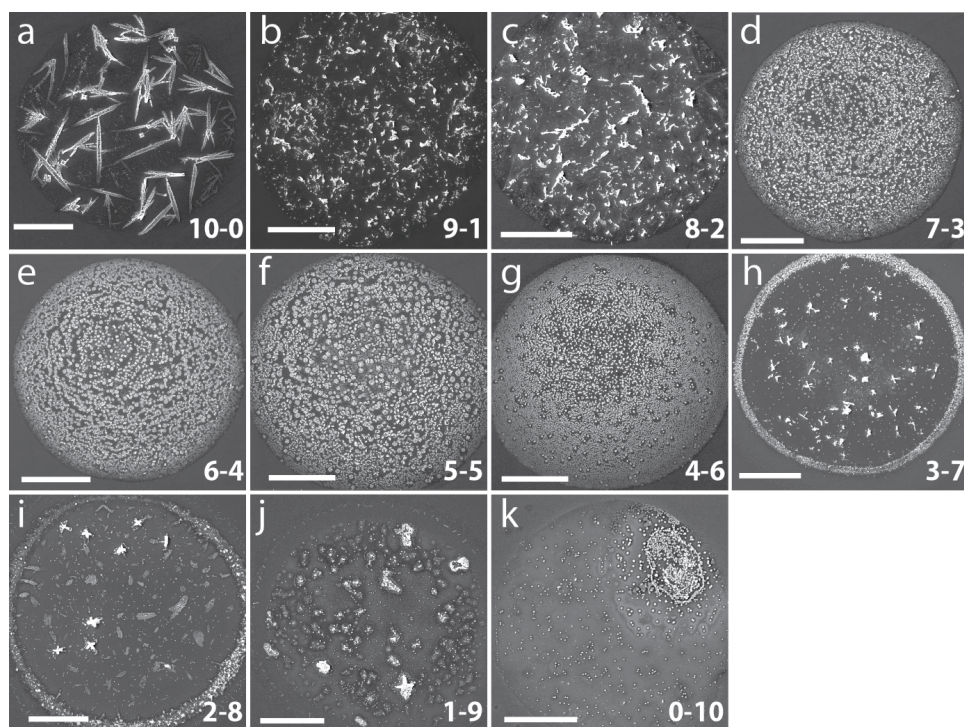


Figure S8. SEM micrographs of varying compositions of Pd-Au. The first number in the lower right of each frame indicates the number of drops of Pd precursor and the second number indicates the number of drops of Au precursor. The compositions range from (a) Pd₁₀-Au₀ to (k) Pd₀-Au₁₀. The white scale bars represent 100 μm . The precursor solutions used for piezodispensing were 0.30 M (NH₄)PdCl₄ and 0.30 M HAuCl₄·3H₂O in ethylene glycol. The films were reduced in flowing 5% H₂/95% N₂ at 350 °C for 1.5 h

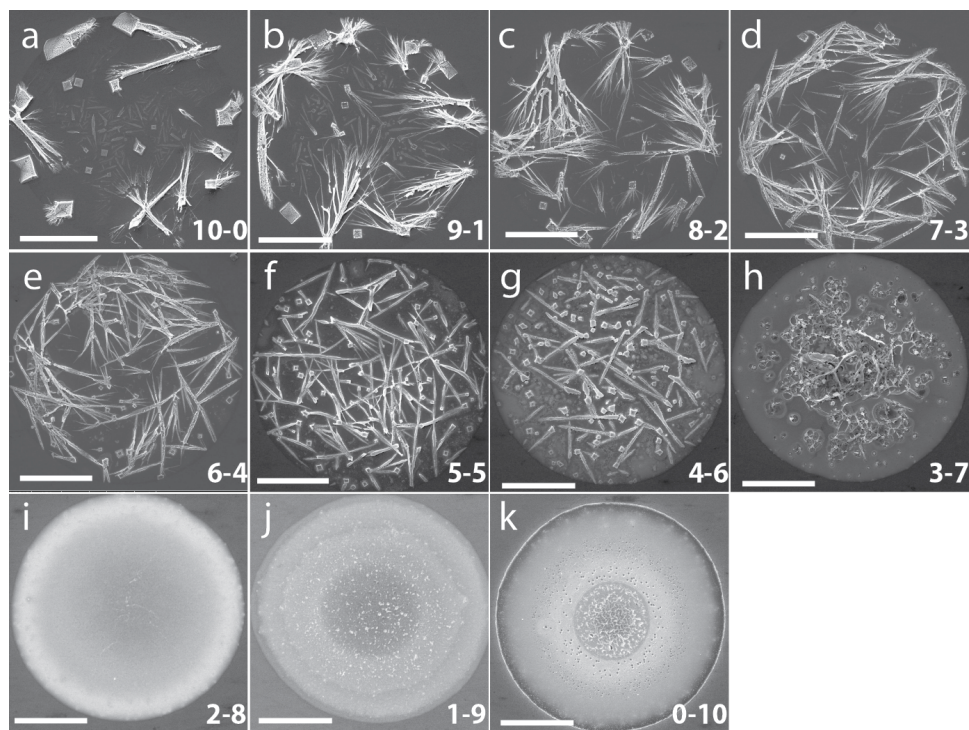


Figure S9. SEM micrographs of varying compositions of Pd-Co. The first number in the lower right of each frame indicates the number of drops of Pd precursor and the second number indicates the drops of Co precursor, from Pd₁₀-Co₀ (a) to Pd₀-Co₁₀ (k). The white scale bars indicate 100 μm . The precursor solutions used for piezodispensing were 0.30 M (NH₄)PdCl₄ and 0.30 M Co(NO₃)₂·6H₂O in ethylene glycol. The films were reduced in flowing 5% H₂/95% N₂ at 350 °C for 1.5 h

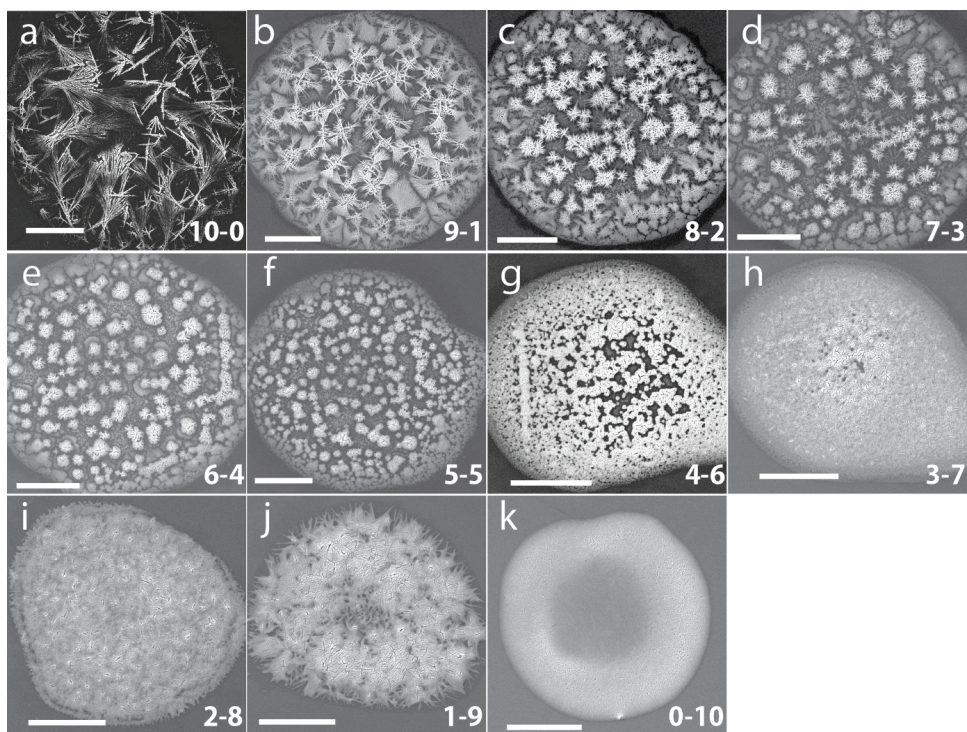


Figure S10. SEM micrographs of varying compositions of Pd-W. The first number in the lower right of each frame indicates the number of drops of Pd precursor and the second number indicates the drops of W precursor, from Pd₁₀-W₀ (a) to Pd₀-W₁₀ (k). The white scale bars indicate 100 μm. The precursor solutions used for piezodispensing were 0.30 M (NH₄)PdCl₄ and 0.30 M (NH₄)₆H₂W₁₂O₄₀·xH₂O in ethylene glycol. The films were reduced in flowing 5% H₂ / 95% N₂ at 350 °C for 1.5 h